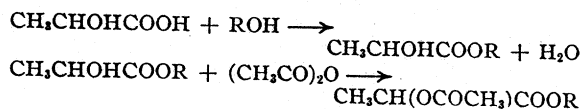


# Pyrolysis of Lactic Acid Derivatives. Production of Phenyl and *o*-Tolyl Acrylate\*

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In recent years considerable interest has been shown in the production of acrylic esters by the pyrolysis of esters of acetoxypropionic acid. These esters can be made from lactic acid by the reactions



Methyl acetoxypropionate<sup>1,2</sup> has been pyrolyzed to give high yields of methyl acrylate. Satisfactory yields of acrylic esters have been obtained also by pyrolysis of the benzyl<sup>1</sup> and tetrahydrofurfuryl<sup>3</sup> esters of acetoxypropionic acid. Other esters of acetoxypropionic acid, including the ethyl,<sup>1</sup> butyl,<sup>1</sup> allyl,<sup>4</sup> and methallyl<sup>4</sup> esters, have been pyrolyzed, but the yields of the corresponding acrylic esters are low, since a predominant side reaction takes place, *i. e.*, the aliphatic alcohol radical is decomposed into the corresponding olefin. For example, ethylene, carbon monoxide, acetaldehyde and acetic acid are formed when ethyl acetoxypropionate is pyrolyzed. Because of this or other side reactions, the satisfactory preparation of acrylic esters by the pyrolytic method appears limited to acetoxypropionic esters that have relatively stable alkyl groups.

Recent work<sup>5</sup> has shown that  $\alpha$ -acetoxyisobutyric esters can be converted by pyrolysis into methacrylic esters more readily than  $\alpha$ -acetoxypropionic esters can be transformed into acrylic esters.

Phenol is thermally stable, and because of their structure phenyl and substituted phenyl esters of acetoxypropionic acid would be expected to be incapable of the side reaction that occurs with ethyl acetoxypropionate and related esters. Results

given in the present paper demonstrate that this expectation was reasonable.

Phenyl and *o*-tolyl acetoxypropionates were prepared by the following series of reactions and also by the methods described in the experimental section: (1) Aqueous 80% lactic acid was acetylated with acetic acid, benzene being used as an entraining agent to remove the water of esterification continuously.<sup>6</sup> The yields of acetoxypropionic acid were as high as 77%. (2) Acetoxypropionic acid was converted by means of thionyl chloride into acetoxypropionyl chloride in 80 to 82% yields. (3) Acetoxypropionyl chloride was converted by treatment with phenol (or *o*-cresol) into phenyl (or *o*-tolyl) acetoxypropionate in yields of almost 90%. (4) Pyrolysis of phenyl acetoxypropionate (or the corresponding *o*-tolyl ester) produced the aryl acrylate (75 to 80% yields).

Phenyl  $\alpha$ -acetoxypropionate was pyrolyzed at temperatures and contact times that ranged from 440 to 600° and from 0.77 to 20 seconds. A pressure of 18 to 19 mm. was used in one experiment, atmospheric pressure for the others (Table I). The yield of acetic acid was always higher than the yield of phenyl acrylate. Carbon monoxide and carbon dioxide were formed in some experiments in considerable amounts. Styrene, obtained in yields as high as 20%, presumably was formed prior to decomposition of phenyl acetoxypropionate into phenyl acrylate since it has been reported by Skraup and Nietzen<sup>7</sup> that phenyl acrylate yields phenol, acetylene, and carbon monoxide on pyrolysis.

*o*-Tolyl acetoxypropionate was pyrolyzed at temperatures ranging from 500 to 591° (Table II). *o*-Tolyl acrylate was obtained in yields as high as 75%; the yields of acetic acid were even higher. No real attempt was made to detect *o*-methylstyrene in the reaction products.

Possibly because of the presence of small amounts of phenol or some other inhibitor, the phenyl acrylate purified by distillation showed little tendency to polymerize. Samples of phenyl acrylate that had been washed with dilute sodium

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(1) R. Burns, D. T. Jones and P. D. Ritchie, *J. Chem. Soc.*, 400-406, 714-717 (1935).

(2) L. T. Smith, C. H. Fisher, W. P. Ratchford and M. L. Fein, *Ind. Eng. Chem.*, **34**, 473 (1942).

(3) H. V. Claborn, U. S. Patent 2,222,363, Nov. 19, 1940; 2,229,997, Jan. 28, 1941.

(4) C. H. Fisher, C. E. Rehberg and L. T. Smith, *THIS JOURNAL*, **65**, 763 (1943).

(5) C. E. Rehberg, C. H. Fisher and L. T. Smith, *ibid.*, **65**, 1003 (1943).

(6) E. M. Filachione and co-workers, "Preparation of Methyl  $\alpha$ -Acetoxypropionate from Lactic Acid, Acetic Acid and Methanol," presented at the Pittsburgh meeting of the American Chemical Society, September, 1943.

(7) S. Skraup and F. Nietzen, *Ber.*, **57**, 1294 (1924).

TABLE I  
PYROLYSIS OF PHENYL  $\alpha$ -ACETOXYPROPIONATE

Expt.	Amount pyrolyzed, g.	Temp., °C.	Contact time, sec.	Ester dec. %	Yields, moles per mole of ester decomposed				
					Acetic acid	Phenyl acrylate	Styrene	CO <sub>2</sub>	CO
77	37	500	18	60	0.65	0.50	..	0.08	0.26
81	49	550	14	96	.81	.64	..	.12	.24
82	39	550	20	100	.88	.66	0.16	.21	.28
84	57	600	10	100	.91	.54	.07	.27	..
90	56	600	6	100	.90	.61	.12	.18	.21
102	56	583	3.7	95	.75	.64	.21	.07	.07
128	45	594	5.5	100	.86	.72	.07	.08	.08
H-170	82	522	19	65	.94	.76	.04	.07	.10
H-172	116	531	12	55	.94	.76	.03	.05	.09
H-173	123	548	15	73	.98	.76	.08	.08	.10
H-174	114	565	12	78	.97	.76	.11	.10	..
H-176	92	440	20	13	.64	.32	..	.01	.14
360 <sup>a</sup>	78	541	0.77	34	.88	.80	..	..	..

<sup>a</sup> A pressure of 18 to 19 mm. was used.

TABLE II  
PYROLYSIS OF *o*-TOLYL  $\alpha$ -ACETOXYPROPIONATE

Expt.	Amount pyrolyzed, g.	Temp., °C.	Contact time, sec.	Ester dec. %	Yields, moles per mole of ester decomposed			
					Acetic acid	<i>o</i> -Tolyl acrylate	CO <sub>2</sub>	CO
134	49	500	15	61	0.83	0.72	0.03	0.09
141	40	547	21	100	.90	.67	.04	.05
363	122	591	7	71	.64	.55	..	..
368	111	542	11	67	.97	.66	..	..
370 <sup>a</sup>	76	549	2.3	82	.97	.75	..	..

<sup>a</sup> A pressure of 18 to 20 mm. was used.

hydroxide solution, however, polymerized readily (mass polymerization at 75°) in the presence of 1% benzoyl peroxide, forming a transparent product that was hard at room temperature but became soft at approximately 60°.

When a sample of *o*-tolyl acrylate isolated from the pyrolysis products by distillation was heated with approximately 1% benzoyl peroxide, a soft and viscous polymer was formed. Samples of the *o*-tolyl ester that had been washed with alkali polymerized readily (mass polymerization at 67°) when treated with 1% benzoyl peroxide. The polymer thus obtained, which was hard at room temperature, softened at approximately 60°.

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#### Experimental

**Preparation of Acetoxypropionyl Chloride.**—A mixture of 4 moles of lactic acid (80%), 28.0 moles of glacial acetic acid, 200 ml. of benzene, and 1 ml. of concentrated sulfuric acid was refluxed, with the continuous removal of water by means of a modified Dean and Stark tube. After twenty-one hours the mixture was neutralized with 4.0 g. of sodium acetate and distilled in vacuum. A 77% yield of acetoxypropionic acid resulted. By heating the acetoxypropionic acid with thionyl chloride (1.1 mole) gradually for approximately two hours to a final temperature of 95°, followed by distilling in vacuum, an 82% yield of acetoxypropionyl chloride was isolated.

**Preparation of Phenyl  $\alpha$ -Acetoxypropionate.**—Phenyl acetoxypropionate was prepared by heating equimolar quantities of phenol and acetoxypropionyl chloride on a steam-bath until evolution of hydrogen chloride ceased. The ester was then isolated in 86 to 88% yields by distillation in vacuum: b. p. 110 to 111° (2 to 3 mm.) and 143° (12 mm.);  $n_D^{20}$  1.4860;  $d_4^{20}$  1.134. *Anal.* Calcd. for C<sub>11</sub>H<sub>12</sub>O<sub>4</sub>: C, 63.45; H, 5.81; M<sub>R</sub>, 52.70. Found: C, 62.63; H, 6.05; M<sub>R</sub>, 52.65.

Phenyl acetoxypropionate was prepared also by (a) the reaction of acetoxypropionyl chloride with aqueous sodium phenolate (65% yield); (b) the interaction of acetoxypropionyl chloride, phenol, and phosphorus oxychloride (30%); and treatment of phenyl acetate with acetoxypropionic acid in the presence of a small amount of concentrated sulfuric acid (45% yield on the basis of unrecovered acetoxypropionic acid).

**Preparation of *o*-Tolyl  $\alpha$ -Acetoxypropionate.**—A mixture of 1.0 mole of *o*-cresol and 1.0 mole of  $\alpha$ -acetoxypropionyl chloride was heated on the steam-bath until evolution of hydrogen chloride ceased. The mixture was then distilled in vacuum, a Claisen flask being used. The *o*-tolyl  $\alpha$ -acetoxypropionate boiled at 112 to 113° below 1 mm.;  $n_D^{20}$  1.4860;  $d_4^{20}$  1.124. *Anal.* Calcd. for C<sub>12</sub>H<sub>14</sub>O<sub>4</sub>: C, 64.85; H, 6.35; saponification equivalent, 111.1. Found: C, 64.01; H, 6.56; saponif. eq., 111.2.

**Pyrolysis.**—The pyrolysis of the acetoxypropionates was carried out by allowing the liquid to run into a Pyrex glass tube having a bore of 30 mm. and heated over a length of 13 inches. The vertical tube, packed with short lengths of Pyrex glass tubing, was heated by an electric furnace<sup>2</sup> controlled automatically. The apparatus<sup>2</sup> was swept with nitrogen before the pyrolysis started and also after all the ester had been added. A small amount of hydroquinone was added to the condensate to prevent premature polymerization.

Titration of the crude pyrolysis product showed the amount of acetic acid present. The acrylate and undecomposed acetoxypropionate were isolated by vacuum

distillation of the crude pyrolysis product. Styrene was also formed in the pyrolysis of phenyl acetoxypionate. It was collected with the acetic acid fraction in the distillation and was isolated by adding salt water to the acetic acid fraction.

Further data on the pyrolysis of phenyl and *o*-tolyl acetoxypionate are given in Tables I and II.

**Properties of Phenyl Acrylate and *o*-Tolyl Acrylate.**—Phenyl acrylate<sup>7</sup> as obtained by the pyrolysis of phenyl  $\alpha$ -acetoxypionate was a virtually colorless liquid that boiled at 63 to 64° at 1- to 2-mm. pressure and 87 to 94° at approximately 12 mm.;  $n_D^{20}$  1.5210;  $d_4^{20}$  1.0762. *Anal.* Calcd. for  $C_9H_8O_2$ : C, 72.97; H, 5.44;  $M_R$ , 41.35. Found: C, 72.77; H, 5.66;  $M_R$ , 41.92. Neither the phenyl nor the *o*-tolyl acrylate polymerized readily until it had been washed with dilute alkali.

The *o*-tolyl acrylate was a virtually colorless liquid: b. p. 55 to 57° at 0.5 mm.; 78 to 79° at 3 mm.;  $n_D^{20}$

1.5160;  $d_4^{20}$  1.050;  $M_R$  (calcd.) 45.96;  $M_R$  (obs.) 46.59.

### Summary

1. Satisfactory methods have been developed for converting lactic acid into  $\alpha$ -acetoxypionyl chloride, phenyl  $\alpha$ -acetoxypionate and *o*-tolyl  $\alpha$ -acetoxypionate.

2. Pyrolysis of the phenyl and *o*-tolyl esters of acetoxypionic acid yielded phenyl and *o*-tolyl acrylate, respectively. Styrene also was formed in the pyrolysis of phenyl acetoxypionate.

3. Relatively hard resins were obtained by polymerizing phenyl and *o*-tolyl acrylate.